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SYNTHESIS AND CHARACTERIZATION OF POLY (O-PHENYLENEDIAMINE) PoPD BY CHEMICAL OXIDATION TECHNIQUE

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Poly (o- phenylenediamine) (PoPD) was successfully synthesized in hydrochloric acid by chemical oxidation method using potassium dichromate as an oxidant. The synthesized polymer was characterized using Raman spectroscopy, SEM, XRD and BET surface area. More unevenly dispersed particles of the Poly (o- phenylenediamine) polymer were observed from the SEM images. The result of the XRD revealed that the sample is amorphous in nature with several minor peaks centered between $2\theta = 15°$ and $2\theta = 17°$. Raman spectra confirmed that the PoPD polymer sample contains phenazine ring ladder – structure made of quinoids and benzenoids imine units. The result from BET showed that the polymer is made up of mesopores due to pore diameter of 2.647 nm obtained by Density Functional Theory (DFT) approach.

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1. Introduction

Intrinsically conductive polymers have become an efficient alternative to inorganic conductors in many practical applications in the recent decade [1]. Polyaniline is an important member of the intrinsically conductive polymers because of the ease of its preparation, an excellent environmental stability, interchangeable oxidation states, electrical and optical properties, economic cost [2, 3, 4] and because they can be used for chemical sensors [5,6], electrochemical and corrosion devices [7, 8]. A good method to obtain soluble conductive polymers is the polymerization of aniline derivatives such as poly (o-phenylenediamine) which was studied in this work. Phenylenediamine belongs to aniline derivatives and PoPD shows different properties when compared to aniline [9]. Poly (o-phenylenediamine) shows different properties when compared to aniline [10]. The derivatives of polyaniline are found applications in different fields like removal of heavy metals from the industrial effluents, anticorrosive agents [11], for studies, microelectronics devices, electromagnetic shielding and in optics [12, 13, 14, 15, 16]. Polymerization of a conducting polymer may be performed with chemical or electrochemical [17] methods. Different chemical oxidizing agents such as potassium dichromate [18, 19], potassium iodate, [20], hydrogen peroxide [21], ferric chloride or ammonium persulphate[22] can 2be used. Different researchers have used different oxidizing agents such as potassium iodate [20], hydrogen peroxide [21], ammonium persulphate [22] among others, but in this work, potassium dichromate was used as the oxidizing agent in the chemical polymerization of (o-phenylenediamine) in aqueous HCl medium. The poly (o-phenylenediamine) obtained was characterized by XRD, Raman, BET surface area, and SEM.

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2. Materials and method

1.622 g of (o-phenylenediamine) (oPD) was added to 50 ml of 0.1M of HCl. The solution was heated and stirred for about 5 minutes. The temperature of the solution was brought down to 20 ^{o}C. Then 50 ml of potassium dichromate ($K_2Cr_2O_7$) was used as the oxidizing agent and was prepared by dissolving 4.413 g of $K_2Cr_2O_7$ in 50 ml of 0.1M of HCl. The dissolved $K_2Cr_2O_7$ was set to drop bit by bit (dropwise) with the help of a burette with a flow rate of 1.43 ml/mins. The solution was left for 24 hrs. Then, the poly (o-phenylenediamine) (insoluble) was separated from the soluble material with the aid of centrifuge and was collected after filteration and repeated washing with distilled water and allowed to dry at a temperature of 50 ^{0}C.

3. Results and discussion

Structural properties of the poly o-phenylenediamine were determined with AR L'X TRA X-ray diffractometer using CuKα (λ=1.54056Å), Raman-L-785-BIS, BET (Quantachrome version 11.03) and SEM (PRO:X:Phenonm world, Model No: 800-o7334). The x – ray pattern of the poly – o – phenylenediamine (PoPD) at 25.0 ℃ with 2 theta angles step of 0.030° and scanning rate of 12.0 $°/min$ is shown in figure 1. The angle ranged from 5.0 ° - 70.0 ° at Cu - $k_{\alpha 1}$ wavelength of 1.5405 Å. The result revealed that the sample is amorphous in nature due to its broad features which is not defined by crystalline model and amorphous materials do not produce sharp diffraction peaks. The pattern is as a result of the incoherent scatter of the x – ray radiation by the molecules of the polymer sample. Several minor peaks centered between 2θ =15 °and 2θ = 17 °.

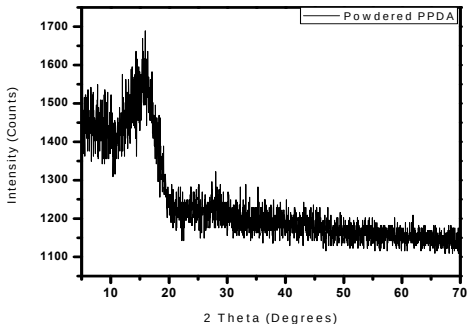

Fig. 1.XRD pattern of powdered PoPD sample.

The bond structure of the synthesized polymer was analyzed by Raman spectroscopy. The characteristic vibrational bands obtained from the Raman spectra of the polymer are shown in Fig. 2. The sample has sharp bands.

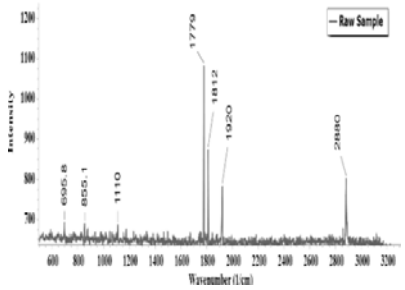

Fig. 2. Raman Spectra of the powdered Poly (o – Phenylenediamine) (PoPD) sample.

Fig. 2 shows the Raman spectra of the powered PoPD. A total of seven bands were observed for the powdered sample. The characteristic vibrational band appeared at 2880 cm^{-1} is due to stretching of aromatic $C-H$ bond, hydrogen bonded amine ($-NH_2$) and ($-NH-$) groups. This confirms the presence of primary and secondary amine functional groups in the synthesized polymer. The pairs of bands at 1920 cm^{-1}, 1812 cm^{-1} and 1779 cm^{-1} are due to stretching vibrations of $C=C$ bond in quinoid and benzenoid rings, and bending vibrations of $C-H$ in quinoid and benzenoid rings respectively. The band at 1110 cm^{-1} is due to $C-N$ stretching frequency of quinoid units and quinoxaline rings. The weak band at 855.1 cm^{-1} is due to out of plane bending deformations of $C-H$ bond present in 1, 2 disubstituted benzene derivatives. The band at 695.8 cm^{-1} is attributed to bending deformation of $N-H$ functional group attached to benzene ring in primary aromatic amines. From the Raman spectra obtained, it was confirmed that the PoPD powdered polymer sample consists of predominantly quinoid, benzenoid rings, and primary and secondary diamine functional group which confirmed that the polymer fabricated contained phenazine ring ladder – structure made of quinoid and benzenoid imine units. The result is in line with spectra obtained by [23, 24, 25, 26, 27]. The produced Poly (o– Phenylenediamine) (PoPD) powder was subjected to surface area, porosity and micropore volume analyses using several approaches.

The surface area analysis of the powdered PoPD polymer was done using Nitrogen as an adsorbate at a temperature of $\approx 77\,K$. $0.14g$ of the sample was subjected to an outgas temperature of 25.0 ℃ in 3.0 $hours$ with a bath temperature of 273.0 K. Two major methods used to determine the surface area analysis were;

(i) Multipoint Brunauer Emmett – Teller (BET) method

(ii) Langmuir method

Other methods such as single point Brunauer Emmett – Teller method, Barret, Joyner and Halenda (BJH) method, Dollimore and Heal (DH) method, t – method, Dubinin – Radashkevich (DR) method and Density Functional Theory (DFT) method.

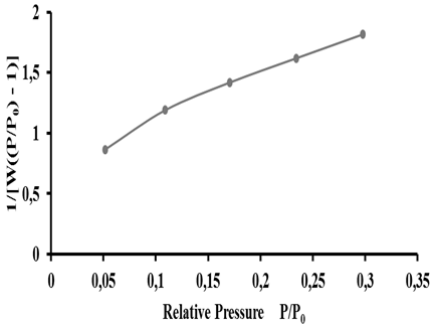

Fig. 3.Multipoint BET plot of the powdered Poly (o – Phenylenediamine) (PoPD) sample.

Fig. 3 shows the multipoint BET plot of the powdered PoPD polymer sample. In the figure, $\frac{1}{\left(W\left\{\left(\frac{P_o}{P}\right)-1\right\}\right)}$ is plotted against $\frac{P}{P_0}$ with the slope and intercept determined. The slope and intercept were used to determine the weight of adsorbate constituting a monolayer of the surface coverage (W_m), the total surface area of the sample (S_t) and the specific surface area of the solid polymer sample (S). The slope (s) of the plot is 3.764 while the intercept (i) is 7.318×10^{-1}, the correlation coefficient (R) is 0.991 and the constant C in the BET's equation is 6.143. The total surface area of the sample is 774.66 m^2/g.

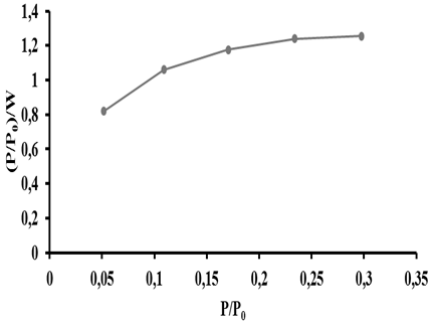

Fig. 4.Langmuir plot of the powdered Poly (o – Phenylenediamine) (PoPD) sample.

Fig. 4 shows the Langmuir plot of the powdered PoPD polymer sample. Langmuir as well as the multipoint BET plot is a linear plot. In the Langmuir plot, $(P/P_0)/W$ is plotted against(P/P_0). The slope, intercept and correlation coefficient were determined.The slope was found to be 1.7497, intercept was 0.8123 and correlation coefficient was 0.930. The surface area according to Langmuir approach is given as $1990.33\,m^2/g$. The Langmuir surface area depends on adsorptions capacity of the adsorbent and is inversely proportional to the molecular mass of the adsorbate only. The Langmuir adsorption model considers that only a monolayer of adsorbate can be formed on top of the sample.Other approaches used in the estimation of the surface area of the sample and their results are presented in Table 1.

Table 1.Surface Area Data for the Powdered PoPD.

Analysis	**Surface Area (m^2/g)**
Singlepoint BET	571.1
Multipoint BET	774.7
Langmuir Surface Area	1990.0
BJH method (cumulative adsorption surface area)	987.6
DH method (cumulative adsorption surface area)	1050.0
t – method (external surface area)	774.7
DR method (Micropore area)	939.0
DFT method (cumulative adsorption surface area)	235.0

3.1. Porosity analysis

Porosity analysis is basically to determine the volume of micropore and pore size created due to the adsorption of the adsorbate by the polymer sample. Porosity or void fraction is a measure of the void or spaces in a material and is a fraction of volume of void over the total volume of the sample. Themicropore volume of the powdered polymer sample was determined using BJH method, DH method, DR method, Horvath – Kawazoe (HK) method, Saito – Foley (SF) method and DFT method. The estimated micropore volumes of the powdered polymer sample using the methods mentioned above are given in table 4. BJH, DH and DFT methods presents cumulative adsorption pore volume while DR, HK and SF methods gave direct values of the micropore volumes based on their individual approaches. The values of the cumulative adsorption pore volume were slightly higher compare to those of direct values of the micropore volume. Fig. 5 shows the Dubinin – Radushkavich (DR) plot of the powdered polymer.

Table 2.Micropore Volume Data for the Powdered PoPD.

Analysis	**Micropore Volume** (cm^3/g)
BJH method (cumulative adsorption pore volume)	0.4766
DH method (cumulative adsorption pore volume)	0.4873
DR method (micropore volume)	0.3337
HK method (micropore volume)	0.1640
SF method (micropore volume)	0.0524
DFT (cumulative pore volume)	0.2720

The pore size of the powdered polymer sample was obtained the methods mentioned above are given in Table 3. BJH and DH measured the adsorption pore diamater of the adsorbent while DR method gave micropore width of adsorbent. DA, HK, SF and DFT methods measured the pore diameter of the adsorbent.

All these semi - empirical methods tend to underestimate the porosity except for density functional theory (DFT) which can describe accurately the configuration of the adsorbed phase at the molecular level. It is considered to be superior and provide a more reliable approach to porosity analysis. According to the density functional theory result, the micropore volume is $0.272\ cm^3/g$ and the pore diameter is $2.647\ nm$. The pore diameter of 2.647 nm according to DFT method suggest that the powdered polymer is made up of mesopores because the value falls within the range of 2 nm and 50 nm which is the standard widths for mesopores.

Table 3. Pore Size Data for the Powdered PoPD.

Analysis	**Pore size**(nm)
BJH method (adsorption pore diameter)	2.072
DH method (adsorption pore diameter)	2.072
DR method (micropore width)	5.555
HK method (pore diameter)	0.366
DA method (pore diameter)	2.740
SF method (pore diameter)	0.452
DFT (pore diameter)	2.647

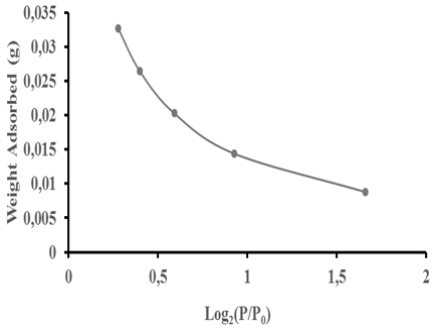

Fig. 5.Dubinin – Radushkavich (DR)plot of the powdered PoPD sample.

Fig. 6 gives the micrograph image of the powdered poly (o – phenylenediamine) sample. The surface of the sample looks rough. More unevenly dispersed particles of the Poly (o - phenylenediamine) polymer were observed. The accelerating voltage of 15 KV and backscatter detector (BSD) were used in determining the SEM image. ImageJ for Microscopy Image Analysis

[28] software was used to determine the average grain size from the micrograph images. Figure 6 shows the micrograph of the powdered PoPD sample taken at 2000 magnification. The SEM analysis of the image showed that the sample has grain sizes ranging from $200\ \mu m - 50\ \mu m$. The sample is made of uneven particle sizes which are in granular form.

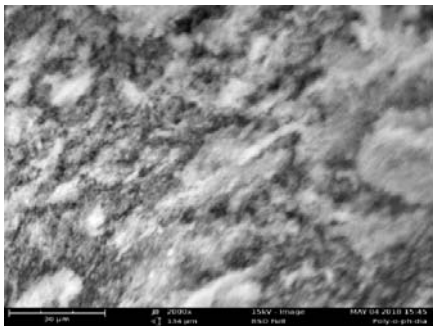

Fig. 6.SEM Micrograph of powdered PoPD films.

4. Conclusions

The synthesis of poly o-phenylenediamine in HCl medium with potassium dichromate as an oxidizing agent using chemical method was successfully achieved. The morphology of the samples was done using scanning electron microscope (SEM) and the structural properties of the samples were determined using X-ray diffractometry (XRD) and Raman spectroscopy. Surface area, porosity and micropore volume analysis of the PoPD were also done using Brunauer - Emmett – Teller (BET).The result of the SEM analysis poly (o – phenylenediamine) sample looks rough

More unevenly dispersed particles of the Poly (o - phenylenediamine) polymer were observed. The result of the XRD revealed that the sample is amorphous in nature with several minor peaks centered between $2\theta = 15°$and $2\theta = 17°$. The result obtained from the Raman spectra confirmed that the synthesized PoPD contains phenazine ring ladder – structure made of quinoids and benzenoids imine units. The result from BET showed that the polymer is made up of mesopores.

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